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A New Crystal Phase of Terephthal-bis-*n*-butylaniline

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Terephthal-bis-*n*-butylaniline (TBBA) is known to present nine phases: one isotropic, one nematic, five smectic, and two crystalline solid phases as shown in Figure 1.[1] A large number of investigations have been made in order to clarify the nature of each smectic phase from various points of view. Recently, Doucet *et al.* have determined the detailed crystal structure of phase VIII (monoclinic system, space group $C2/c$, and unit cell dimensions $a = 53.2$ A, $b = 5.75$ A, $c = 17.57$ A, and $\beta = 115.47°$) and also the lattice constants of the low-temperature phase IX at $-50°C$ (triclinic system, $a = 26.8$ A, $b = 5.75$ A, $c = 17.52$ A, $\alpha = 83.5°$, $\beta = 121.2°$, and $\gamma = 96.5°$).[2]

In the course of the calorimetric study of this material, we have found a new crystalline phase at much lower temperature, which is briefly reported in this paper.

TBBA obtained from Tokyo Ōka Kogyo Co. Ltd. was purified by recrystallization three times from hot ethanol. The thin platelike single crystals precipitated were dried under high vacuum at room temperature. The crystal VIII-to-smectic V phase transition occurred at 113.3°C.

Heat capacity measurements were made at 1° intervals from $-185°C$ to room temperature by using an adiabatic scanning calorimeter (Sinku Riko SH-2000L). The result is given in Figure 2. It should be noticed that a new endothermic peak appears at $-174°C$. The enthalpy and entropy changes of this peak are 0.067 kcal mol^{-1} and 0.68 cal mol^{-1} $°K^{-1}$, respectively. This peak is sharp in a virgin sample as is seen in Figure 2, but disappears if once the specimen is heated up to the smectic V phase. We have confirmed this peak to be due to a reversible crystalline transformation by X-ray diffraction method. Figure 3 shows the X-ray counter curves at the diffractions angles

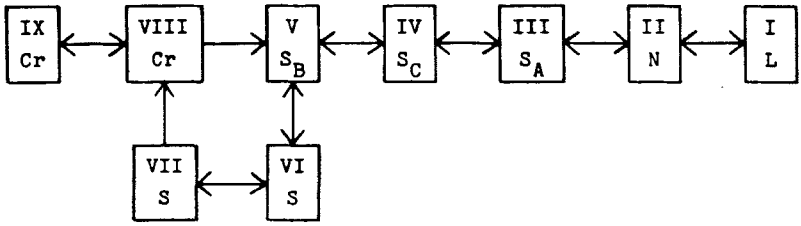

FIGURE 1 Schematic diagram of polymorphism for TBBA.

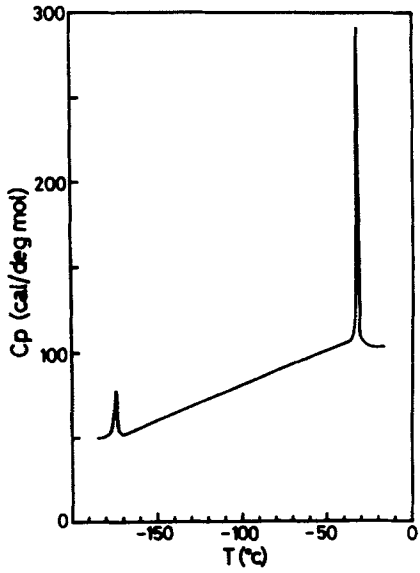

FIGURE 2 Heat capacity of TBBA.

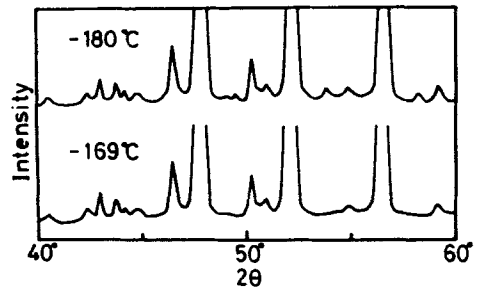

FIGURE 3 X-ray counter curves of TBBA taken at −180 (upper) and −169°C (lower).

$40° \leqslant 2\theta \leqslant 60°$ taken at -180 and $-169°C$ with the incident beam normal to the b axis of the TBBA crystal. On the upper curve there appear several weak reflections which can not be observed on the lower curve of phase IX. This figure suggests that these two modifications assume the essentially similar crystal structures. The details will be presented elsewhere. Thus, it has been turned out that TBBA exhibits a total of ten phases above liquid nitrogen temperature. The 10-th phase must be added to the schematic diagram of polymorphism for TBBA shown in Figure 1. The nature of this phase and the origin of its transition are not clear at present.

The IX-to-VIII phase transition is observed at $-33°C$ and the heat of transition is found to be 0.3 kcal mol^{-1}. These values are just in agreement with the data given in Ref. 2. It has been proposed that this phase transition is due to a rotational relaxation involving the end tails of the TBBA molecule.[3] In terephthal-bis-ethylaniline and terephthal-bis-*n*-propylaniline no crystalline transformation has been observed within temperature range investigated here. It may be suspected from these results that the phase transition corresponding to the transition at $-33°C$ in TBBA also occurs in the homolog with the longer *n*-alkyl group. In fact, two phase transitions have been detected at -42 and $-25°C$ in terephthal-bis-*n*-hexylaniline.[4]

Further thermal and X-ray studies on the homologous series of terephthal-bis-*n*-alkylaniline are now in progress.

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